2017 DOE AMR Review

Vehicle Technologies Office

Advanced Emission Control for High-Efficiency Engines

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Project Overview

Timeline

- 2009 – 2019
- 3-Year Renewal Executed – March 2016
- Finish – March 2019

Budget

- Matched 50/50 by Cummins as per CRADA agreement
- DOE funding for FY16 – FY19: $300K each year.

Barriers

- Lack of cost-effective emission control
- Durability of emissions control devices
- Low temperature performances

Partners

- Pacific Northwest National Laboratory
- Cummins, Inc.
  - w/Johnson Matthey

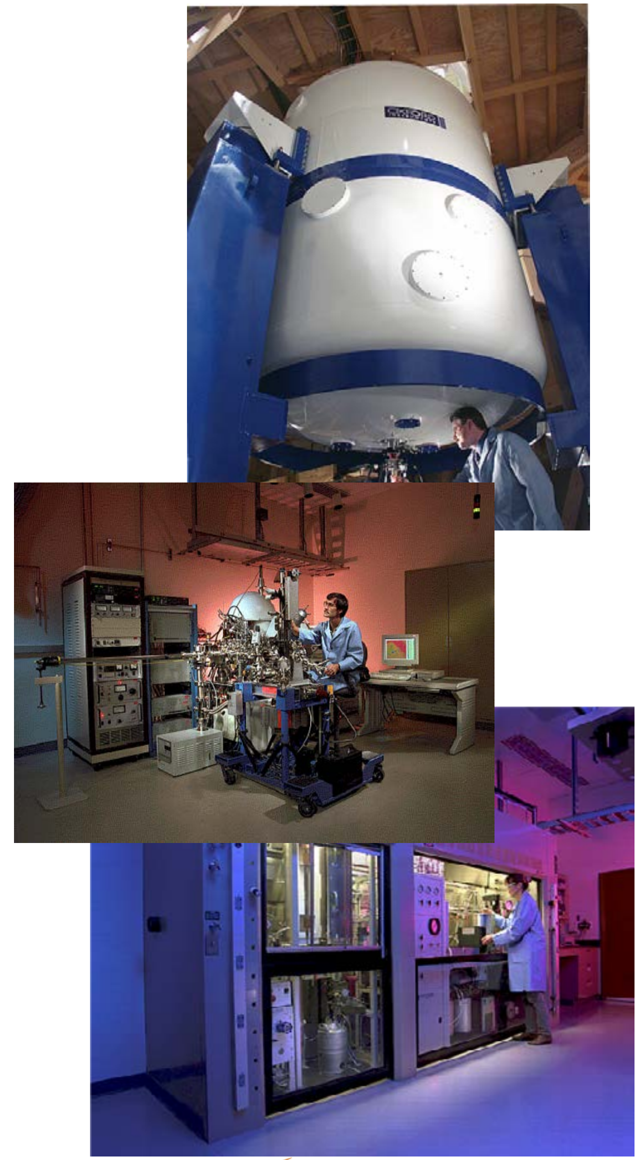
Goals and Objectives

Focus on a broad and very important area of critical relevance to DOE and Cummins: Advanced emission control for high-efficiency engines

- Passive NOx absorbers - Develop next generation materials to address the cold-operation, as driven by improved engine efficiency.
- Oxidation of methane and short alkanes – Address cold-operation emissions arising from CNG vehicles.
- Improved understanding of particulate matter (PM) – Understand the properties of exhaust PM as a function of engine operating conditions and aftertreatment.

Approach

- Taking advantage of the strengths from the partners:
  - Johnson Matthey: Catalyst formulation and upgrading.
  - Cummins: catalysis laboratory with on-engine testing.
  - PNNL: state-of-the-art catalyst characterizations
- Fundamentally understand the relationship of particulate properties and engine operation/aftertreatment utilizing unique approach for *multidimensional* real-time *in-situ* characterization of individual exhaust particles.
- Revealing fundamental aspects of the chemistry and catalytic materials involved in PNA and small alkane catalytic oxidation.



Milestones

1.0	**Passive NOx Absorber**			
1.1	Prepare Pd-loaded zeolite catalysts: different Pd loading methods (incipient wetness, ion exchange) on three different zeolite structure (small pore (SSZ-13), medium pore (ZSM-5) and large pore (Beta)).	PNNL	June, 2016	√
1.2	Determine PNA properties of all zeolites prepared (NOx uptake/release experiments).	PNNL/Cummins	Mar., 2017	√
1.3	Complete initial studies of NOx storage/release mechanisms in Pd-loaded zeolites (kinetic and spectroscopy studies).	PNNL	Mar., 2018	On track
1.4	Evaluate thermal stability and resistance to poisons (S, HCs) of all Pd-loaded zeolites PNA materials.	PNNL	Mar., 2019	Not started
2.0	**Methane and Ethane Oxidation at Low Temperature**			
2.1	Elucidate deactivation mechanisms of supported Pd catalysts	PNNL	June, 2017	On track
2.2	Evaluate non-precious metal based catalysts	PNNL/Cummins	Mar., 2018	Not started
2.3	Study the effects of sulfur on catalyst activity and stability	PNNL/Cummins	Mar., 2019	Not started
3.0	**Improved understanding of particulates**			
3.1	Instrument deployment at Cummins Filtration (Stoughton, WI) and exhaust PM characterization	PNNL/Cummins	April, 2016	√
3.2	Data processing and reporting	PNNL/Cummins	Dec., 2016	√
3.3	Data analysis to guide the development of PM emission control strategies and representative laboratory test protocols for the evaluation of durability and reliability of electronic exhaust sensors.	PNNL/Cummins	Mar., 2019	Not started

Technical Accomplishments

- Passive NOx Absorber
  - Finished synthesis, characterization and evaluation of the first series of catalysts (Pd/ZSM-5, Pd/Beta, Pd/SSZ-13) formed via ion exchange.
  - Finished preparation of the second series of catalysts via incipient wetness impregnation. Characterization and evaluation undergoing.
- Methane and Ethane Oxidation at Low Temperature
  - Evaluating a large group of Pd and Pt catalysts supported on various supports including Al_2O_3, CeO_2, CeO_2-ZrO_2, ZSM-5, Beta and SSZ-13. Will choose promising ones for detailed studies on deactivation mechanism and its prevention.
- Improved understanding of exhaust PM
  - Comprehensively characterized chemical and physical properties of individual exhaust particles emitted during more than 80 operating conditions, including different running cycles, 2 aftertreatment systems, sampling at different points of the aftertreatment systems (engine out, DPF out, SCR out).
  - Completed data processing and identified particles with various sizes, shapes, morphologies, and compositions

PNA Materials

Increasing pore size

Catalyst	Si/Al	ICP Pd (wt.%)	Pd/Al	Na^+ Exchangeable Pd(%)
Pd/Beta_0.50%	12.5	0.50	0.04	75.0
Pd/Beta_0.92%	12.5	0.92	0.07	11.2
Pd/ZSM-5_0.48%	15	0.48	0.04	73.8
Pd/ZSM-5_0.62%	15	0.62	0.06	65.3
Pd/SSZ-13_0.50%	12.5	0.50	0.04	1.4
Pd/SSZ-13_0.88%	12.5	0.88	0.06	9.1

- NH_4/zeolites with $PdCl_2$ (Sigma-Aldrich, Pd(II)Cl_2 ≥ 99.9%) solution (0.5 or 1 wt.% based on parent zeolite mass, pH = 5 adjusted using NH_4OH) for ~ 70h under stirring at room temperature, followed by washing, drying at 120 °C in N_2 for 5h and then calcination at 550 °C for 5h.
- Zeolite structure greatly influences Pd dispersion.

PNA: Pd Dispersion Probed with STEM

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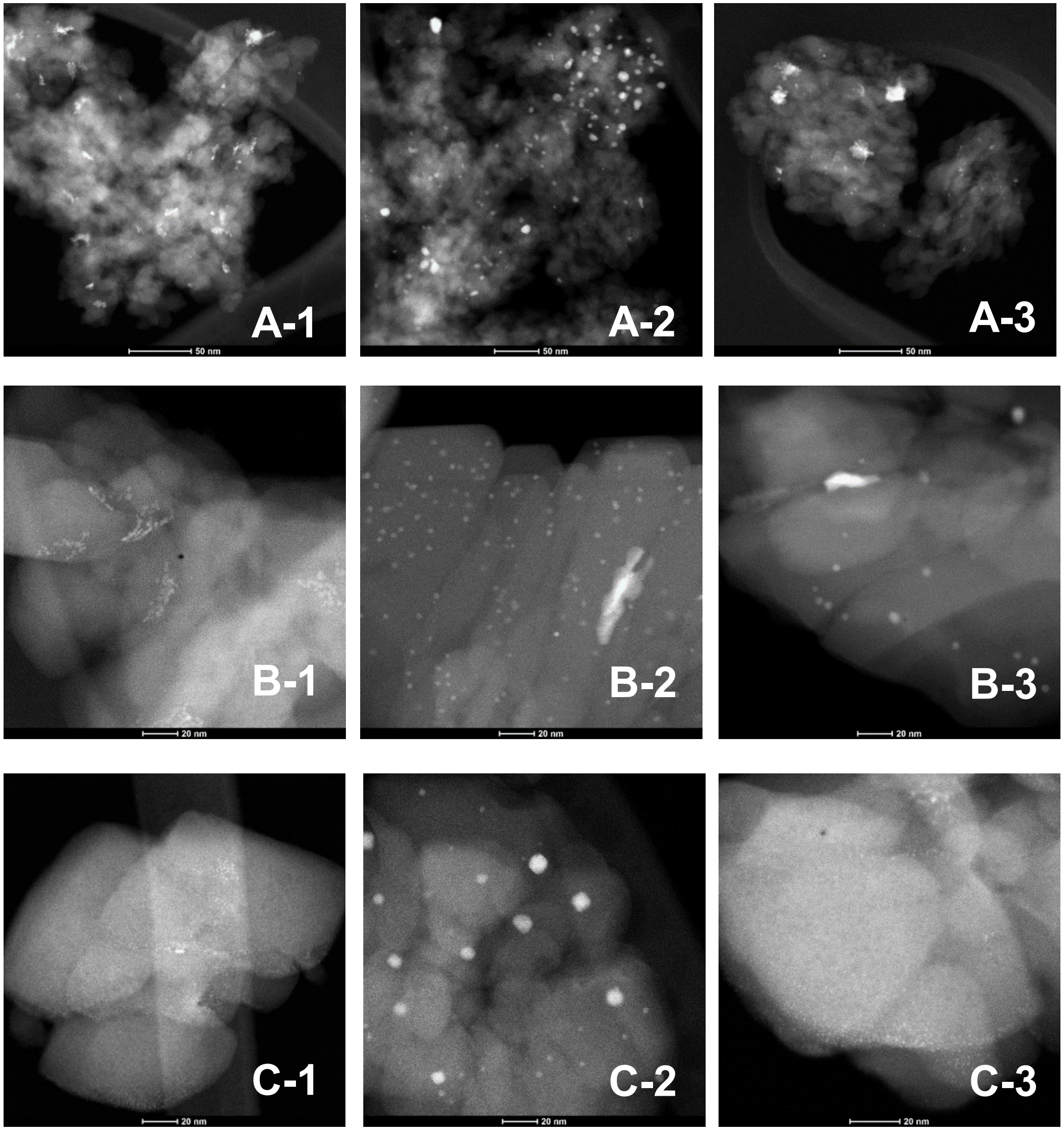
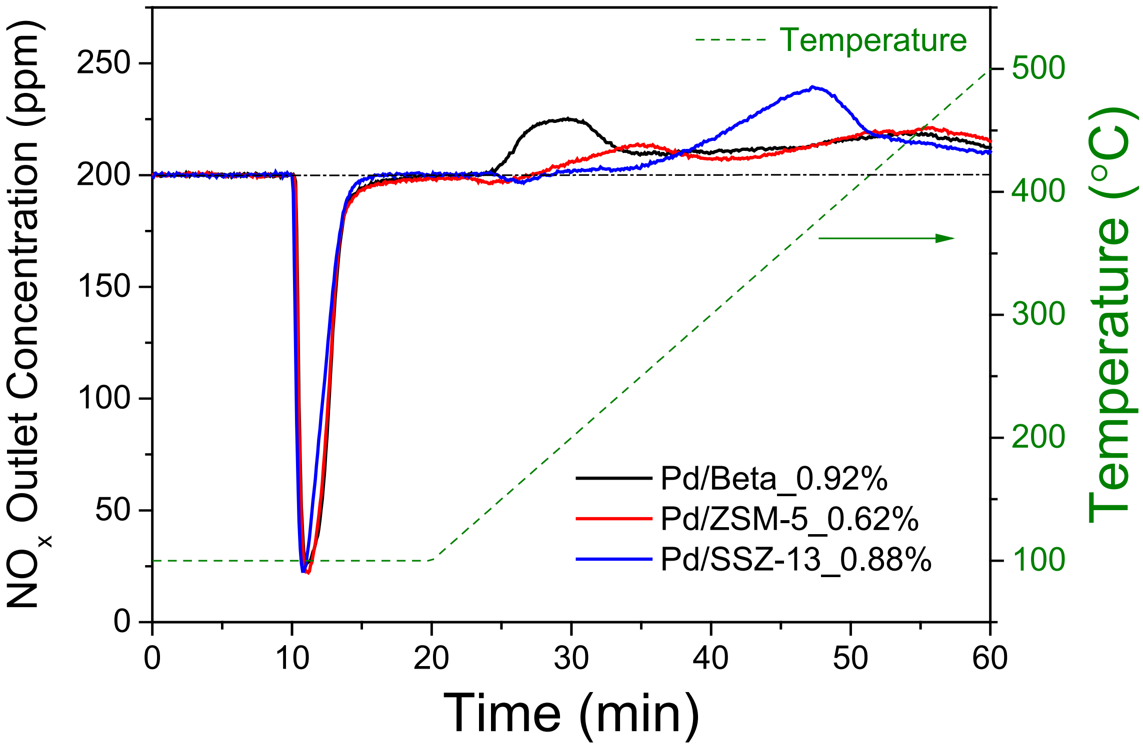
Fresh	Reduced at 400 °C in H_2	Reoxidized at 500 °C in O_2	
			Pd/Beta 0.92%
			Pd/ZSM-5 0.62%
			Pd/SSZ-13 0.88%



- Pd clusters formed after reduction, except few on Pd/ZSM-5.
- PdO redispersed after oxidation.

PNA: NO_x Adsorption and Release Depend on Zeolite Structure, Feed Composition, Temperature



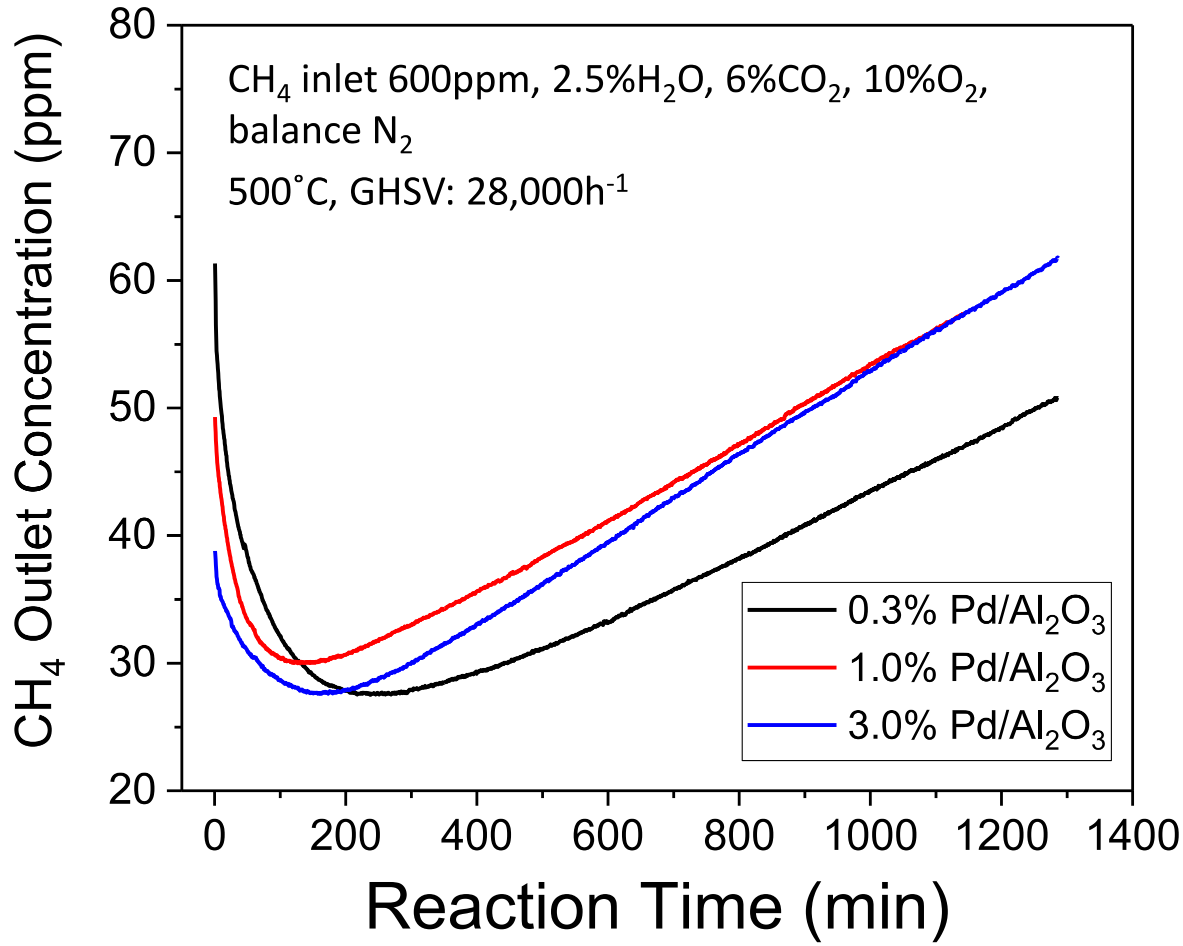
200 ppm NOx (185 ppm NO + 15 ppm NO_2), 200 ppm CO, 14% H_2O, 2.5% H_2O balanced with N_2.

Adsorption at 100 °C for 10 min, then ramp to 500 °C to release trapped NOx.

NOx/Pd ratio during NOx trapping at 100 °C for 10 min

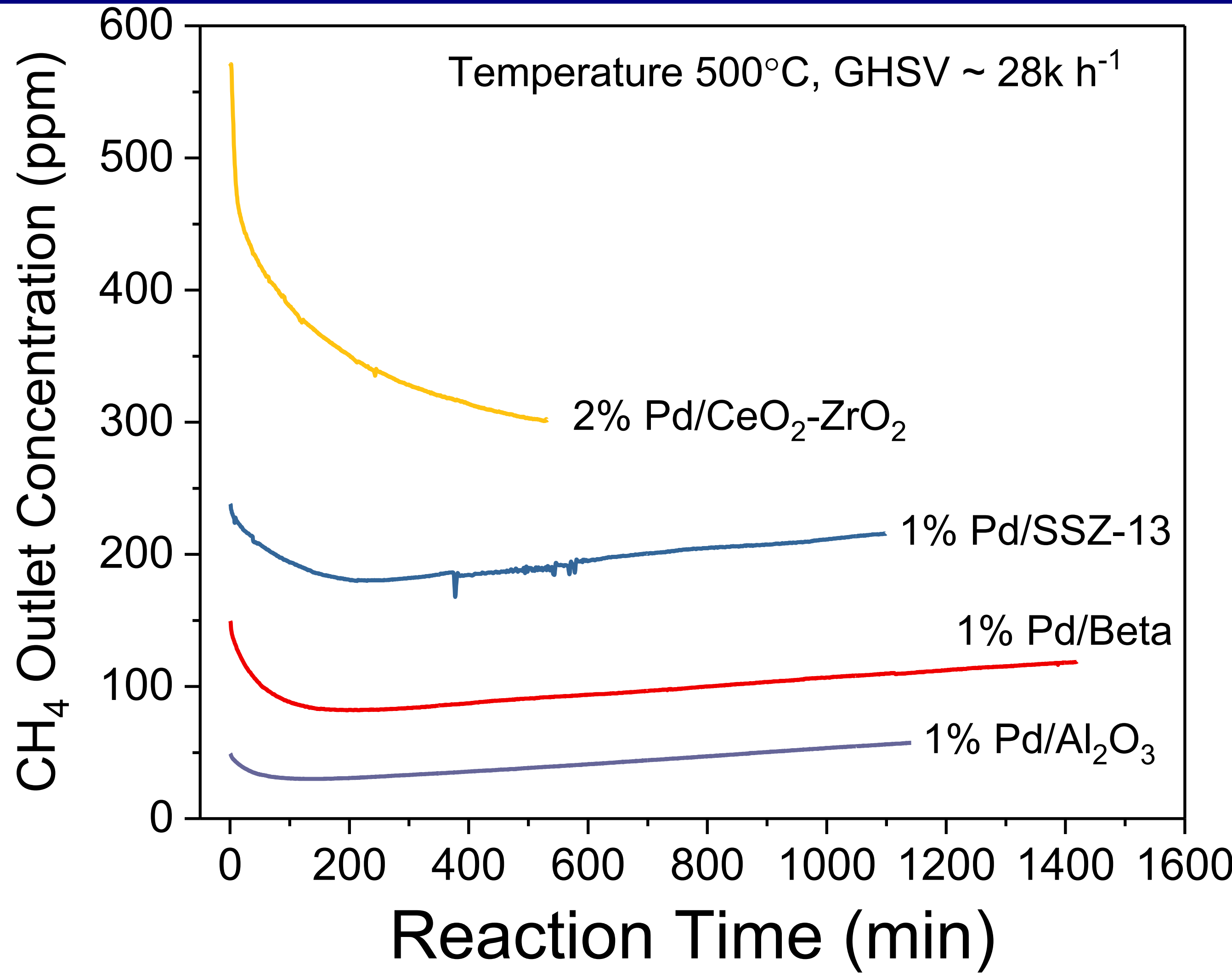
	Dry 200 ppm NOx feed	200 ppm NOx + 2.5% H_2O feed	200 ppm NOx + 200 ppm CO + 2.5% H_2O feed
Pd/Beta_0.92%	1.26	0.28	0.51
Pd/ZSM-5_0.62%	0.88	0.50	0.70
Pd/SSZ-13_0.88%	1.08	0.14	0.44

Methane Oxidation: Baselined the Performances of Pd/Al_2O_3



- JMC equivalent baseline Pd/Al_2O_3 catalysts were prepared.
- Typical induction and deactivation behaviors were observed (Ciuparu *et al.*, *Catal.Rev – Sci. & Eng.*, 2002, 44, 593-649; Fujimoto *et al.*, *J.Catal.*, 1998, 179, 431-442).
- Deactivation could be due to metal sintering or –OH inhibition (Schwartz *et al.*, *JPCC*, 2012, 116, 8587-8593) which will be future studies.

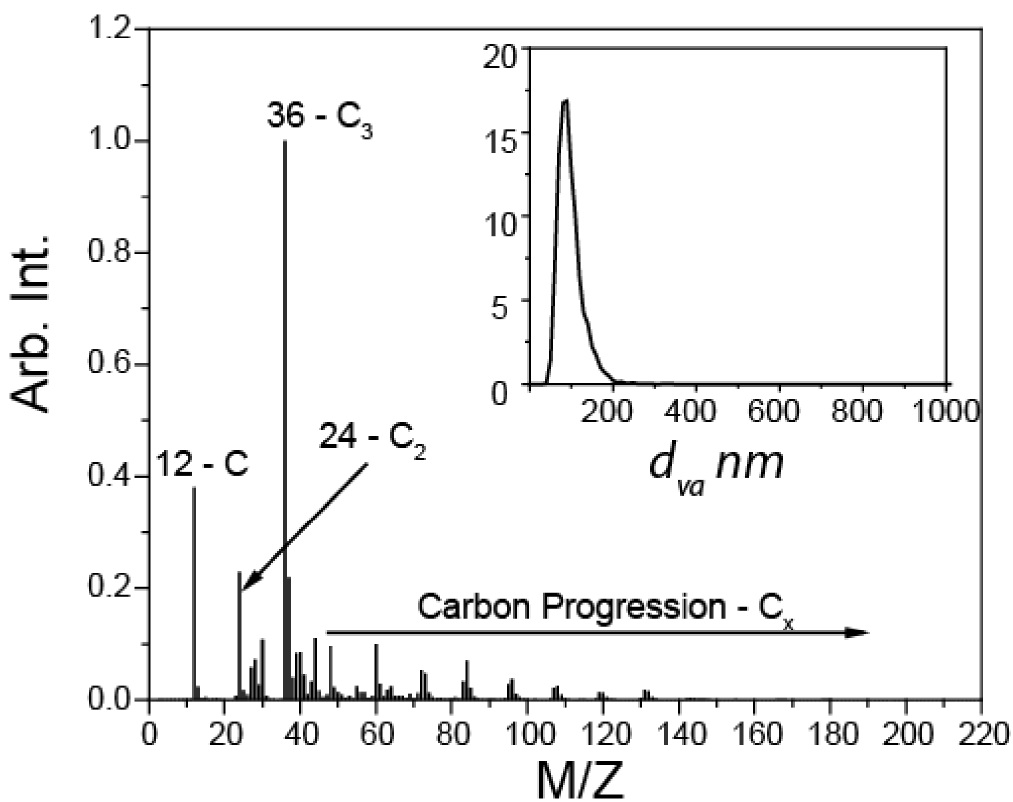
Methane Oxidation on Pd: Al_2O_3 Outperforms Other Supports

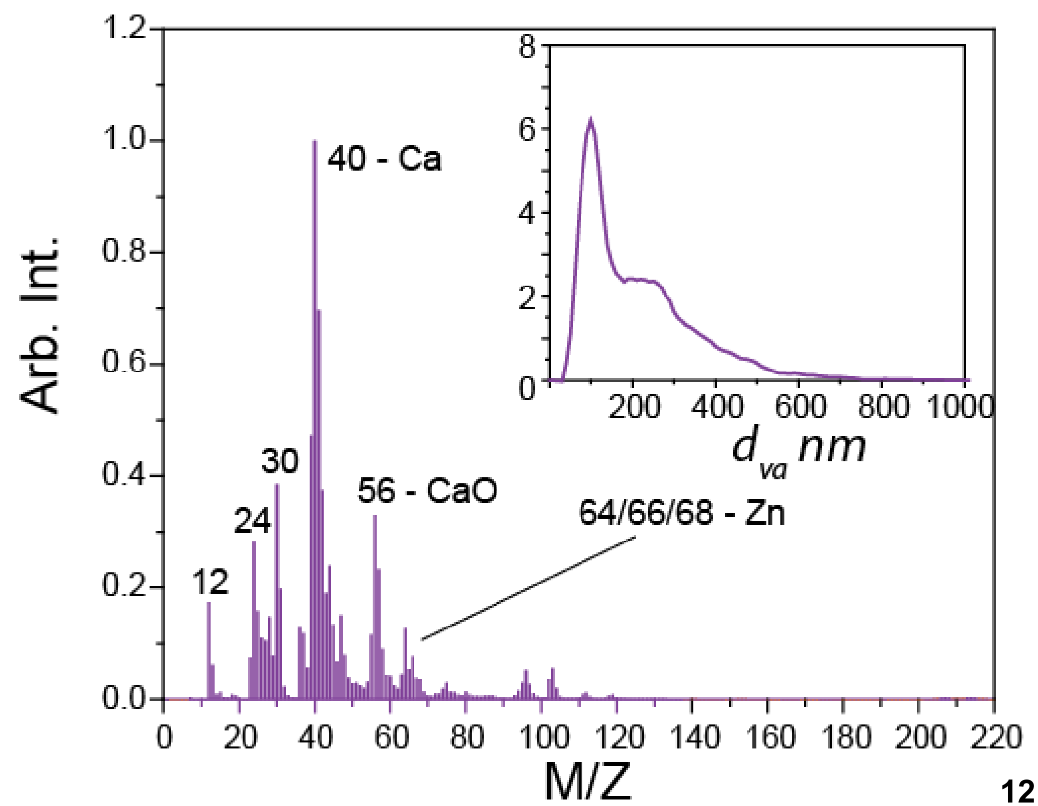


- Zeolite supports do not show advantages in the fresh form. Hydrothermally aged form will be studied.
- Pd-Pt and Pd-Au alloys may have interesting properties in terms of resistance to deactivation.

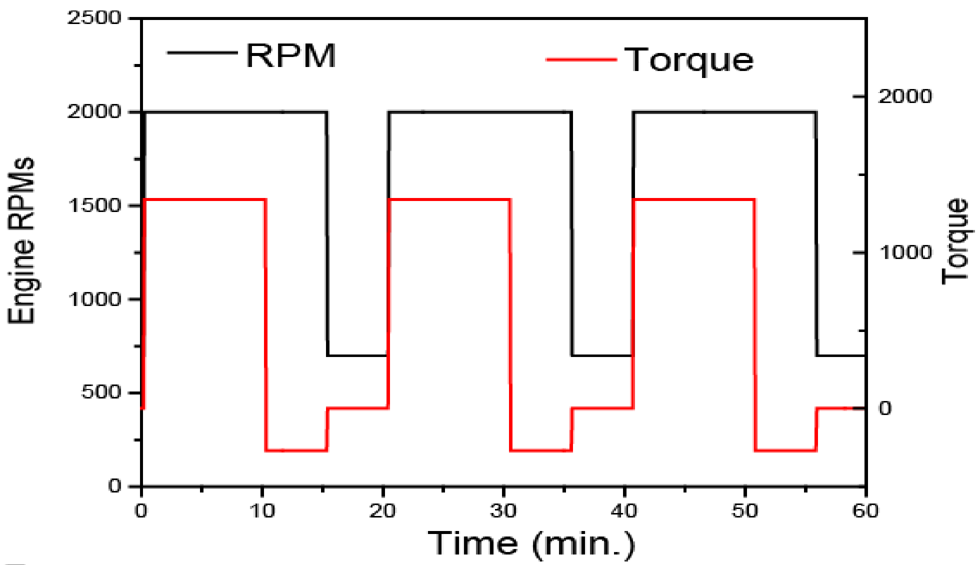
Improved Understanding of Exhaust PM

- Exhaust PM represents a complex mixture of particles with various sizes, shapes, morphologies, and compositions.
- Virtually all particles are internally mixed, but a number of different particle types/classes can be identified, including fractal soot particles, ash, particles dominated by oxygenated organics, nitrates, metals, etc.
- Example below: fractal soot particles and ash-containing particles with corresponding size distributions.
- Abundance of different particle types strongly depends on operating conditions (e.g. speed, load) and the aftertreatment system.

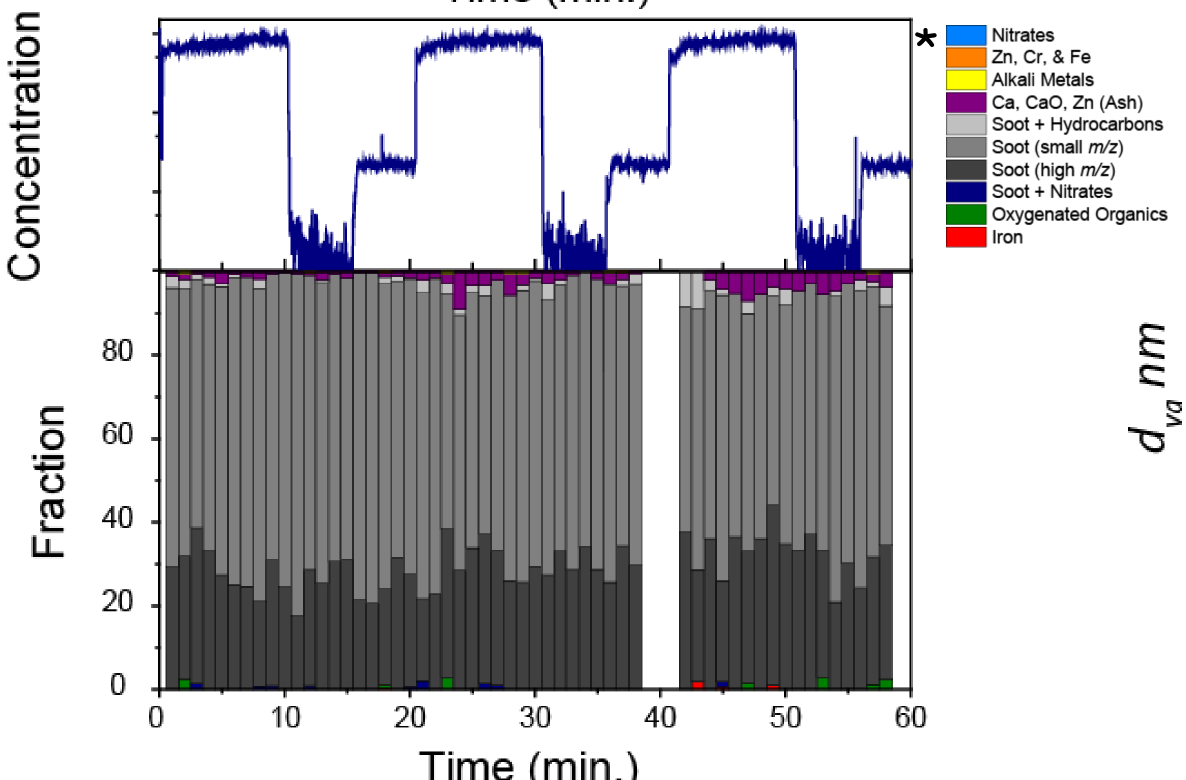


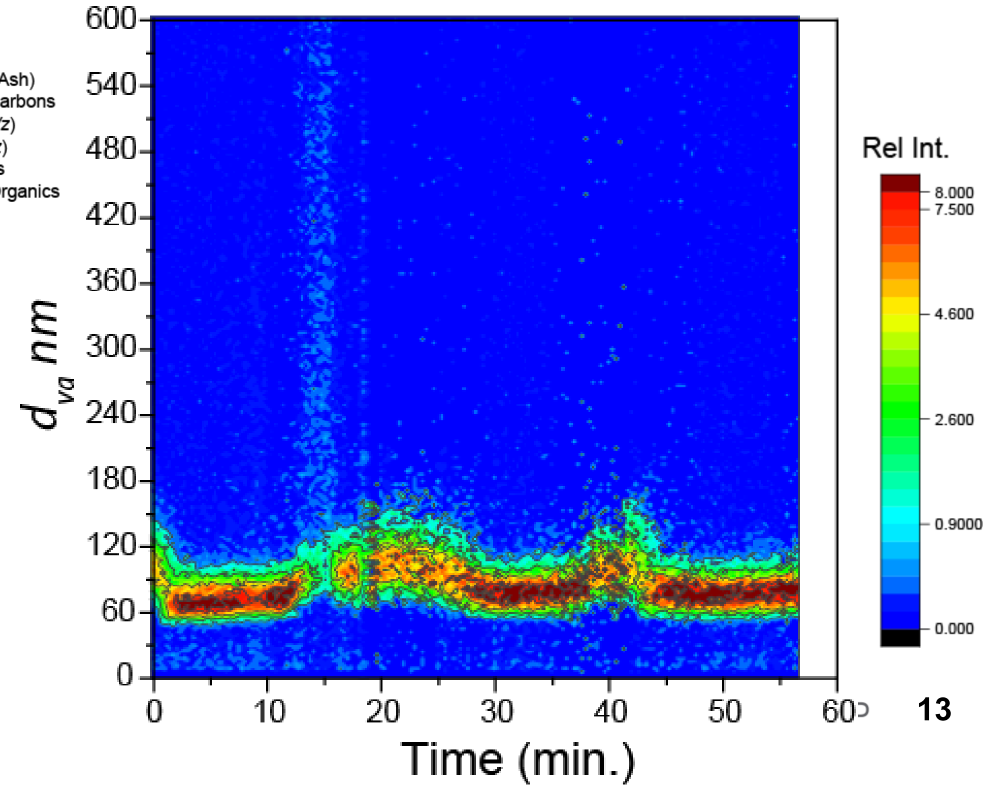


Improved Understanding of Exhaust PM: Engine Out



- PM properties (number concentrations, compositions, size distributions, morphologies) strongly depend on engine operating conditions and the aftertreatment system.
- Engine out PM is dominated by fractal soot particles and contains small fraction of ash particles.





* *The names of particle classes do not represent the exact particle compositions*

Improved Understanding of Exhaust PM: New DPF

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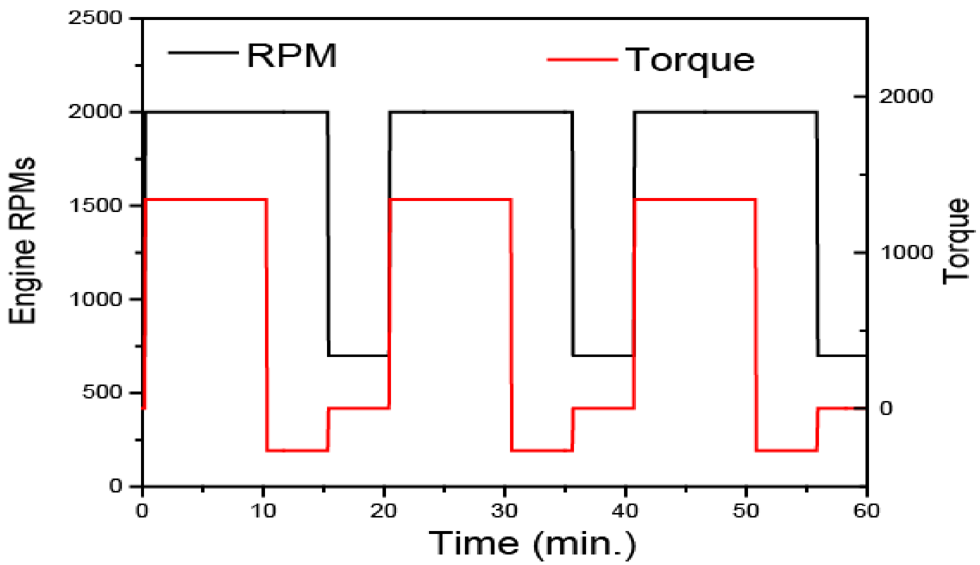
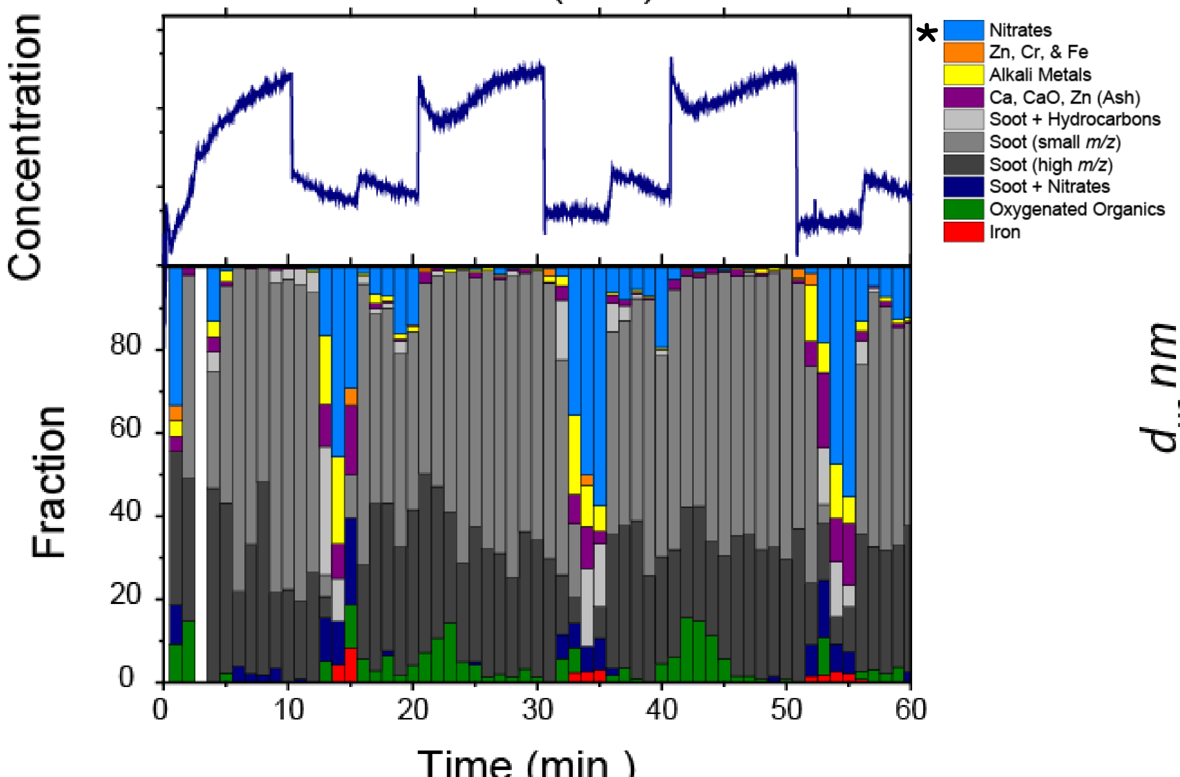
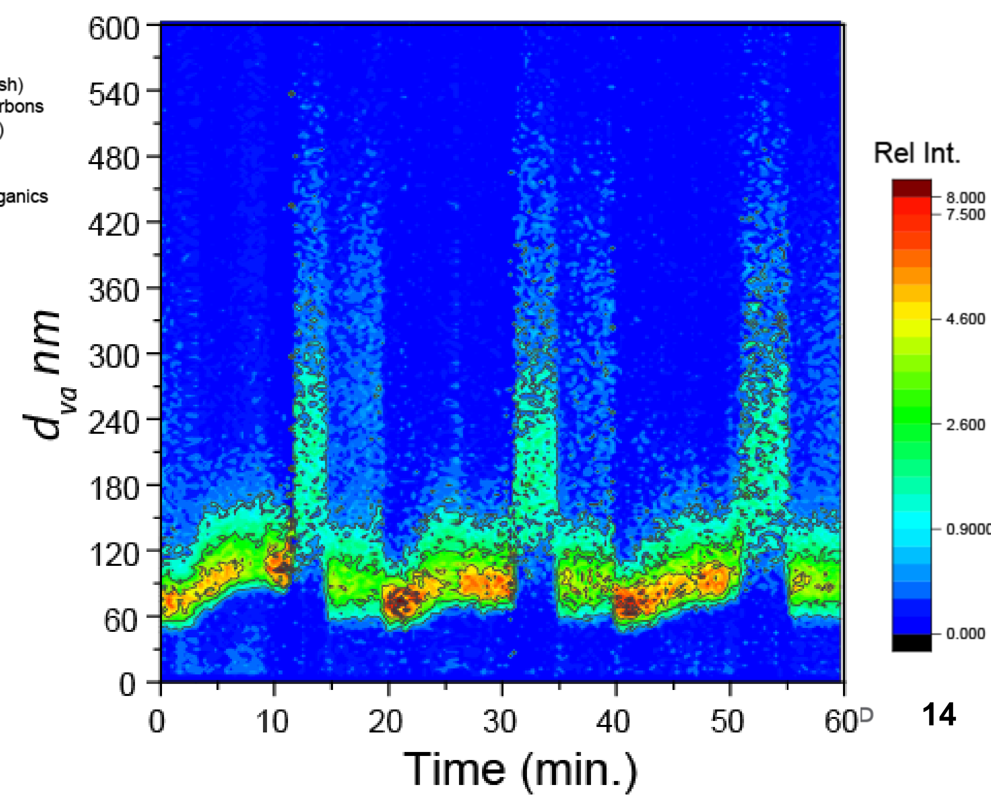


- PM properties strongly depend on operating conditions and the aftertreatment system.
- DPF drastically reduces PM number concentrations, affects PM compositions, size distributions, morphologies
- High speed/high load conditions produces mostly fractal soot particles, while high speed/low load results in large fraction of larger, compact particles composed of nitrates, ash, and metals





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Improved Understanding of Exhaust PM: Aged DPF/SCR

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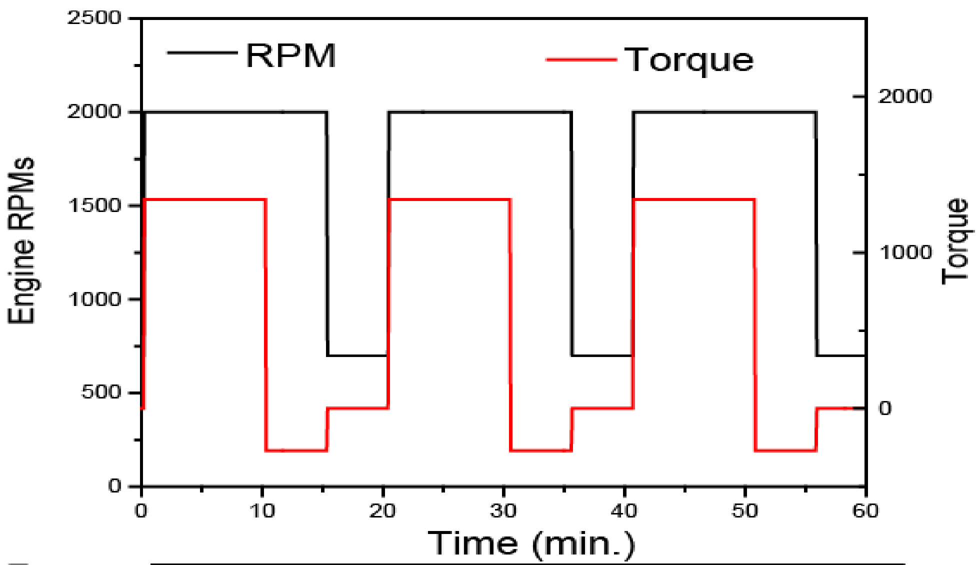
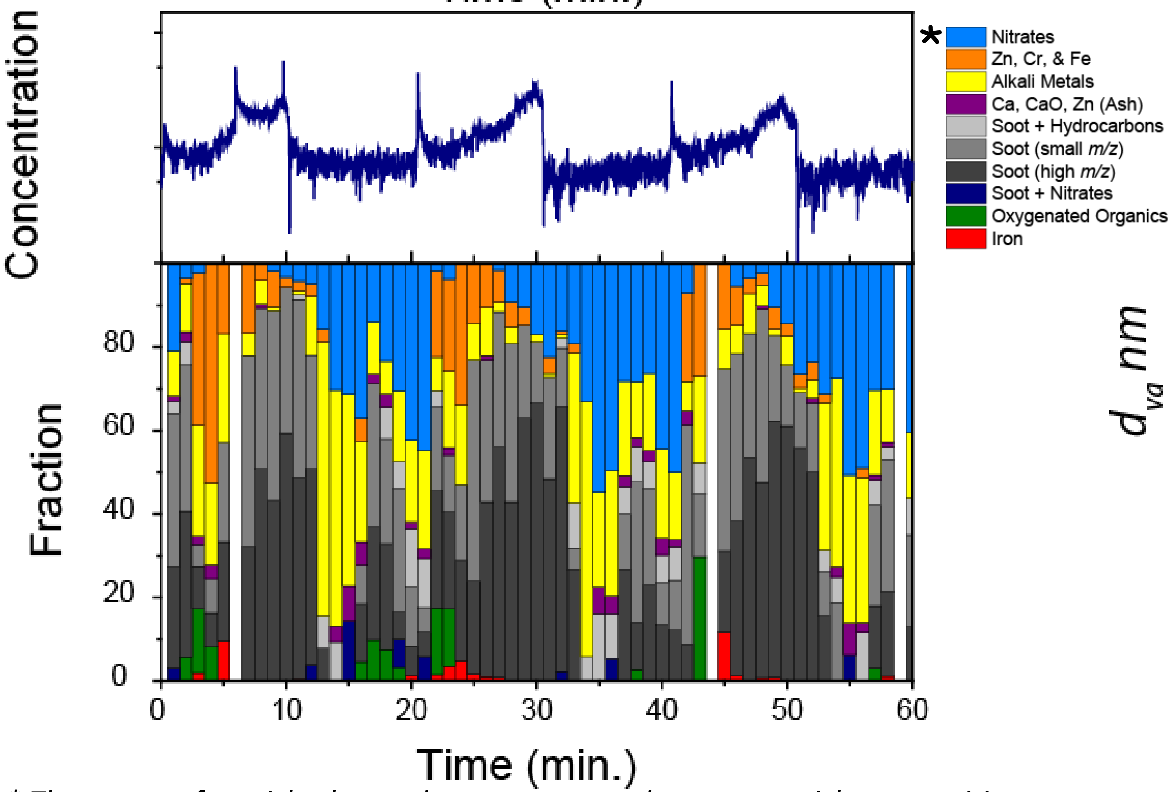
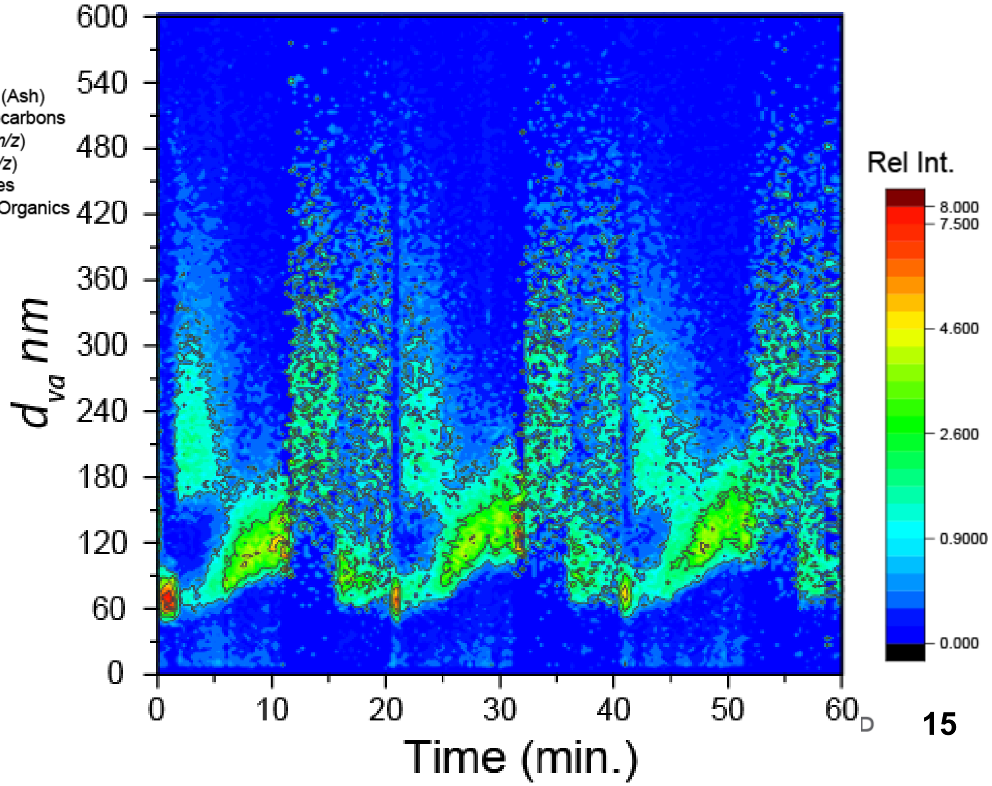


- PM properties strongly depend on operating conditions and the aftertreatment system.
- Old DPF/SCR aftertreatment drastically reduces PM number concentrations, affects PM compositions, size distributions, morphologies
- Low load conditions produces large fraction of larger, compact particles composed of nitrates, ash, and metals

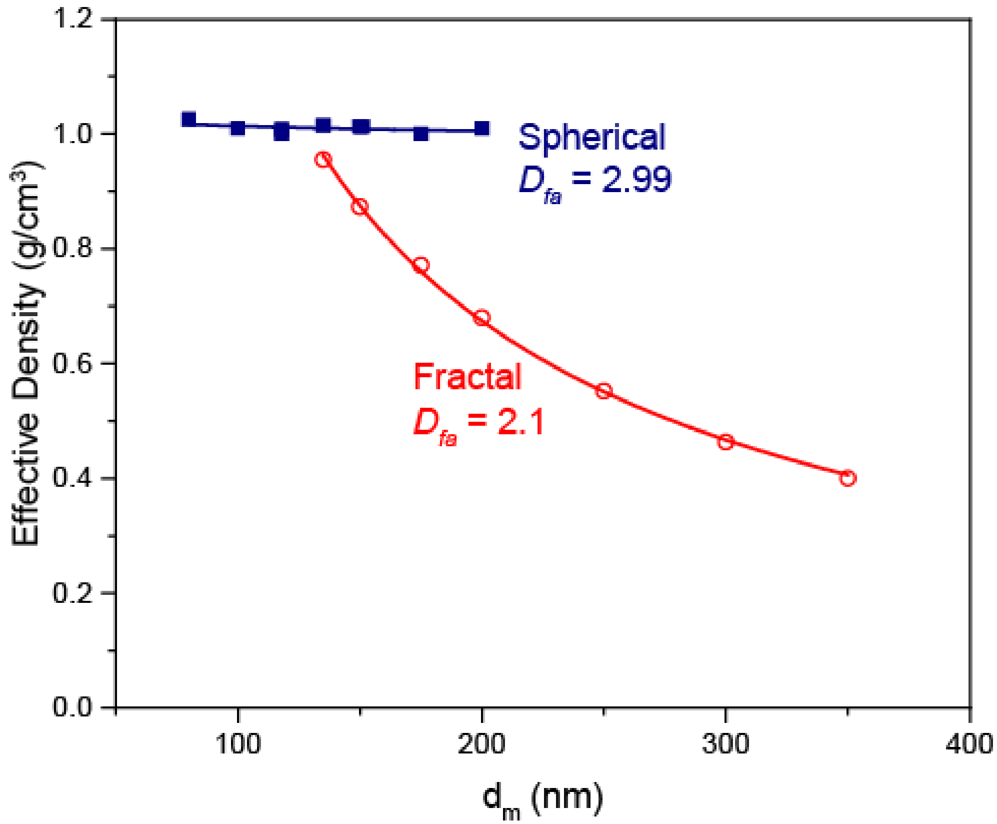


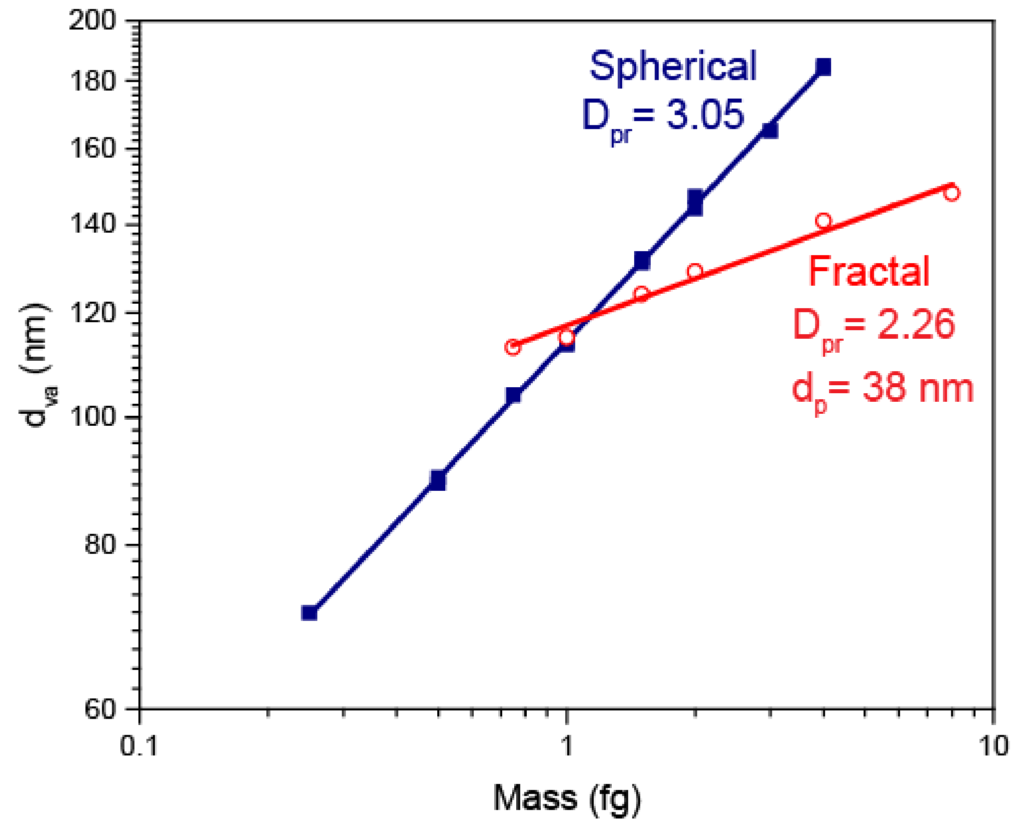


* *The names of particle classes do not represent the exact particle compositions*

Improved Understanding of Exhaust PM: Steady State

- PM properties strongly depend on operating conditions and the aftertreatment system.
- Under some conditions we identified particles with the same mass or mobility diameter that have very different properties. For example, under steady state B50 Engine out condition PM is dominated by 2 particle types: spherical organic particles with density of ~ 1 g/cm^3 and fractal soot agglomerates that comprised of primary spherules with average diameter of 38 nm and have fractal dimension of 2.1.

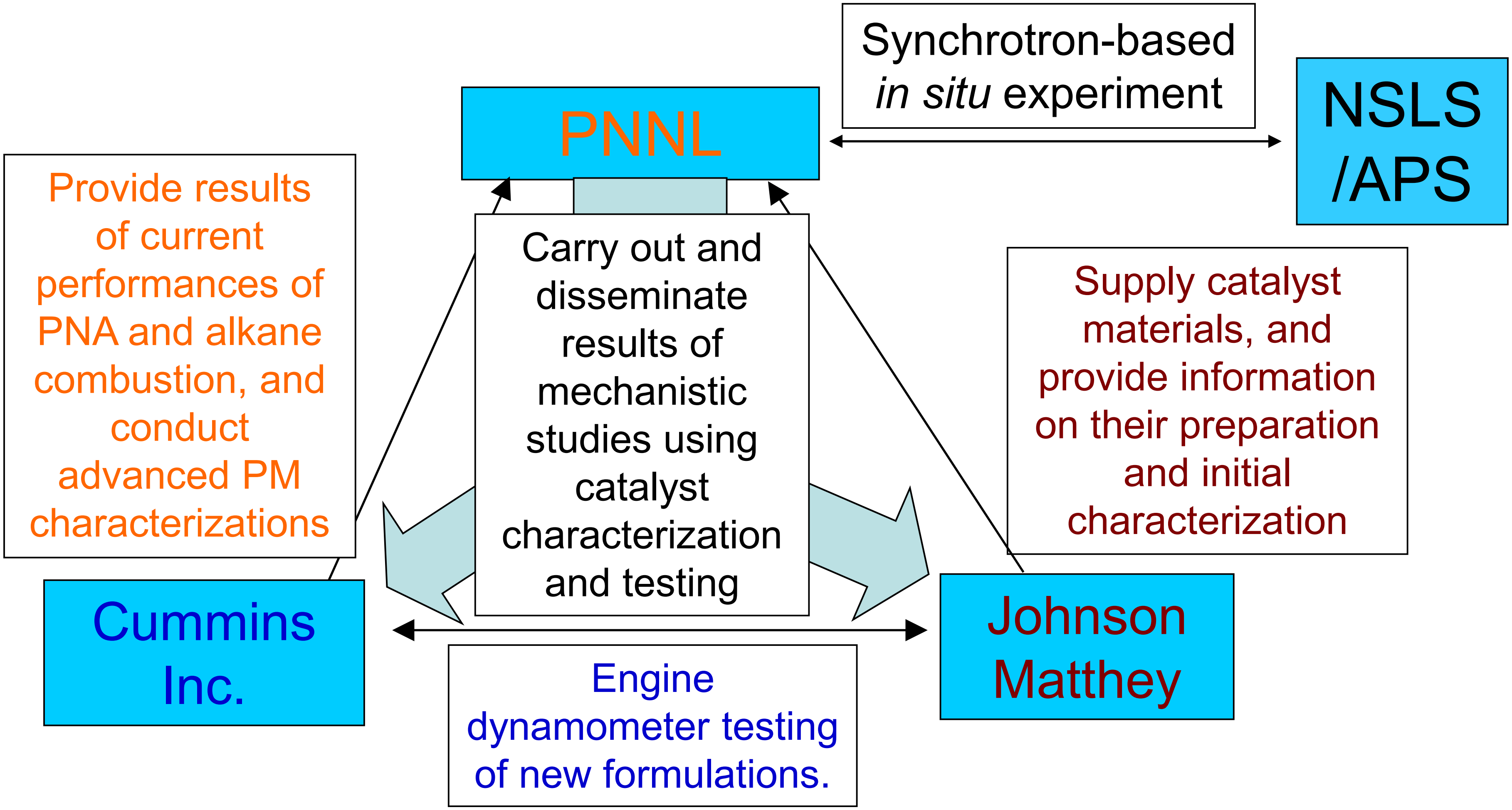




Response to Reviewers' Comments

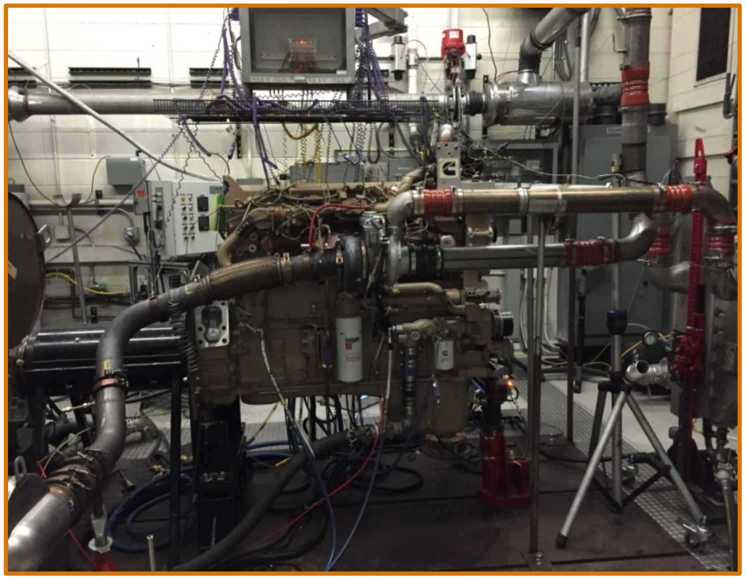
New project, started in March 2016, was not reviewed in 2016 AMR.

Collaborations/Interactions

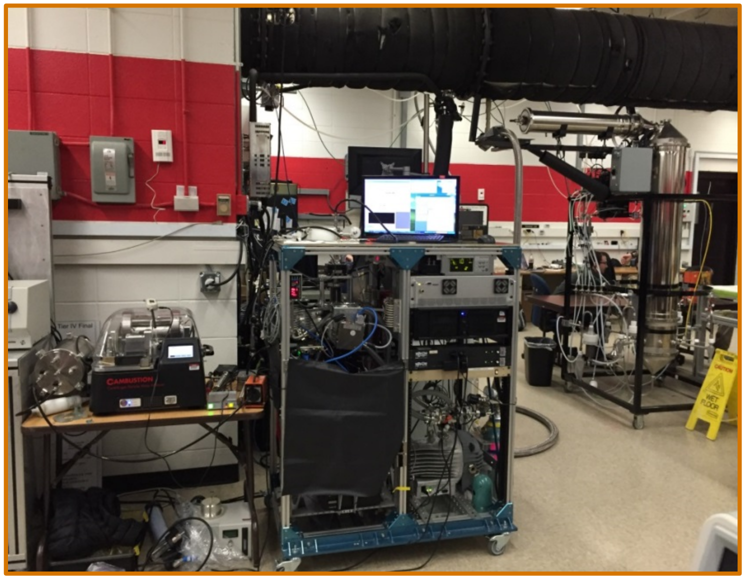


- Conference calls are held monthly to discuss the results.
- Annual face-to-face CRADA Review was held in Columbus, IN. (Dec. 2016)

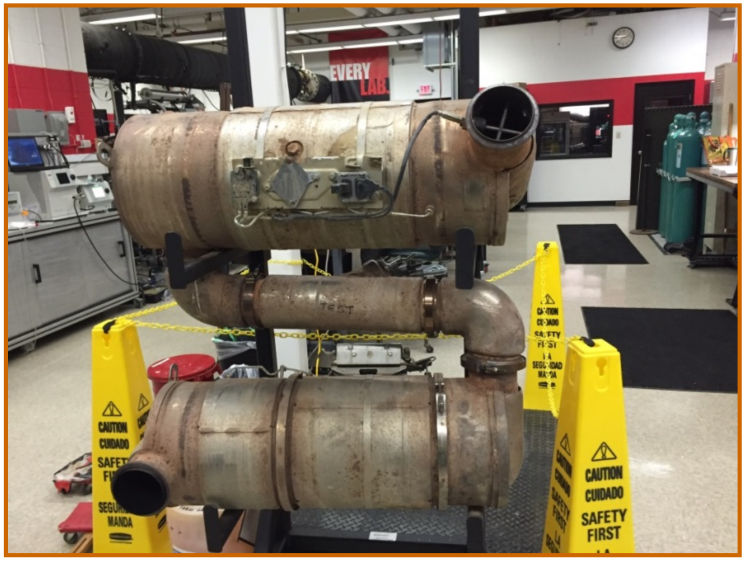
Improved Understanding of Exhaust PM: Collaborative Study at Cummins



2016 Cummins ISX Diesel Engine



PNNL's unique PM characterization system deployed at Cummins



Cummins's new and aged aftertreatment systems (DPF/SCR)

- During two-week collaborative study that took place at Cummins Filtration we comprehensively characterized individual exhaust particles emitted during more than 80 operating conditions (different running cycles, 2 aftertreatment systems, sampling at different points of the aftertreatment systems (engine out, DPF out, SCR out), etc.
- Conference calls are held periodically to discuss the results

Planned Future Work

PNA:

- Hydrothermal aging effects for the PNA catalysts.
- Sulfur and HC tolerance for the PNA catalysts.
- *In situ* synchrotron based studies on PNA catalysts.

Low-Temperature Methane & Ethane Combustion:

- Detailed studies on deactivation mechanism and its prevention.
- Alloying effects in combustion: Pd-Au and Pd-Pt.

Improved understanding of particulates:

- Data analysis to develop understanding of the relationship between engine operating conditions/aftertreatment and PM physicochemical properties and establish laboratory test protocols for the evaluation of durability and reliability of exhaust sensors.

Any proposed future work is subject to change based on funding levels.

Summary

PNA:

- First generation and second generation PNA materials prepared via solution ion exchange and incipient wetness impregnation.
- Strong zeolite structural effects on Pd dispersion: pore opening restriction found on SSZ-13.
- NOx trapping efficiency influenced by nature of Pd (nuclearity and oxidation state). Atomic dispersion and lower oxidation states facilitates NOx trapping. NOx release temperature depends on zeolite structure: smaller pore opening, higher release temperature.

Low-Temperature Methane & Ethane Combustion:

- Reproduced deactivation behavior of Pd/Al_2O_3 catalysts in CH_4 combustion reported in literature. Identified proper approaches to understand this deactivation behavior, including in situ/in operando DRIFTS and STEM.
- Pd and Pd-alloy supported on other materials, especially zeolites, are also under investigation.

Improved understanding of particulates:

- One-of-a-kind approach for *multidimensional* real-time *in-situ* characterization of individual exhaust particles provided unique insights into chemical and physical properties of emitted PM. This knowledge is critical for the development of strategies to address the tightening emission regulations and their enforcement for exhaust PM.